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THE DESIGN AND TESTING OF AN AUTOCLAVE SYSTEM FOR LIGNIN HYDROTREATING

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ABSTRACT

The objective of this task is to prepare a system in which catalysts, found effective in the conversion of lignin model compounds into low-molecular-weight phenols, suitable as feedstocks for methyl aryl ethers, can be tested with lignins. A stirred autoclave system has been built that incorporates the most important features found in the literature for the effective hydrotreating of lignin into low-molecular-weight phenolics. An injection system is included that allows lignin suspensions to be input into the autoclave preheated to hydrotreating temperatures. The collection system is set up so that volatile products may be swept from the autoclave to prevent their possible further reaction. The autoclave system has been tested with lignins using a hydrogenolysis reaction. Injection of aqueous lignin suspensions into the preheated autoclave worked well. The system operated well at high temperature and at pressures far in excess of those necessary for hydrotreating. A lignin-derived oil was produced in good yield from experiments lasting 5 and 20 minutes. The oils were phenolic in nature and may possibly be used as pasting oils in the future.

THE DESIGN AND TESTING OF AN AUTOCLAVE SYSTEM FOR LIGNIN HYDROTREATING

INTRODUCTION

As part of the overall objective to achieve a cost-effective conversion of lignins into methyl aryl ethers, this work has concentrated on the engineering aspects of hydrotreating lignins in a bench-scale reactor. A system has been built in which lignins may be hydrotreated to phenols, using the most promising catalysts identified in the experiments with model compounds (see Ratcliff et al., this Proceedings). These catalysts are designed to have dual functionalities, mild deoxygenation with some hydrocracking ability so that phenols with small alkyl side chains are produced. Catalysts are also being selected that minimize direct hydrogenation to prevent formation of saturated hydrocarbons such as cyclohexane and derivatives, that excessively consume hydrogen. The autoclave system has been designed to preserve the high selectivity of the catalysts being developed in the other part of this task.

From our review of the literature (Chum et al., in press), a number of important features were identified that should be included in any reactor design for the hydrotreating of lignin. Our own experience from hydrotreating lignin in a small tubing bomb reactor was in agreement with these observations, and so a system has been built with a 300 mL stirred autoclave that incorporates these features. Some preliminary experimentation has been carried out with this system to check its operation at high pressure and temperature and to determine our ability to obtain good mass balances on material injected.

This report details the design and experimentation performed to date using this autoclave. Prior results in the tubing bomb reactor have been reported (Ratcliff et al., in press).

Design of Lignin Hydrotreating System

From the survey of the literature we carried out in FY 85, we identified a number of design characteristics common to all the most successful lignin hydrotreating reactors. The heating rate applied to the lignin slurry should be rapid so that hydrotreating temperatures (370°-450°C) are reached quickly (1-2 minutes). If exposed to intermediate temperatures for extended periods, undesirable reactions, e.g., condensations, could take place, making the conversion of lignins to low-molecular-weight phenolics more difficult. A high rate of mixing is also desirable so that the hydrogen gas, catalyst, and lignins are in intimate contact. This also helps provide a more uniform temperature profile, preventing "hot spots" from occurring. Removal of the phenolic products from the reactor as rapidly as possible was also shown to be important to prevent further reaction to products that were excessively hydrogenated or to increased yields of char. All these features were incorporated in the ebullated bed reactor used by Hydrocarbon Research Inc. (HRI) in which the largest pilot-scale studies of lignin hydrotreating were performed (Gendler et al., 1983). Ebullated bed reactors, however, consume large amounts of material, on the order of 0.5 kg per hour. The preliminary catalyst screening should be carried out on, at most, 0.2 kg of lignins from a

practical point of view. An ebullated bed reactor exists at Colorado School of Mines, Department of Chemical Engineering, which may be used in the future. It will require at least 3 kg of lignin per run and will be used in later pilot-scale studies to generate more realistic data for the economic evaluation of this process.

The results from the early work in this project using the small tubing bomb reactor (Ratcliff et al., 1987) were also in good agreement with our observations from the literature. The tubing bomb reactor was set up so that it was rapidly heated to hydrotreating temperatures by raising a preheated fluidized sand bath around the reactor. Mixing was provided by attaching the reactor to a mechanical shaker and augmented by placing two steel balls inside the reactor. The setup was designed to run in either truly batch mode or with a flow of hydrogen through the reactor allowing us to sweep out volatile products into a collection system. The continuous removal of products was found to be very important, resulting in yields of phenols five times that obtained in the true batch experiments and reducing char (tetrahydrofuran insolubles) yields by a factor of two.

Consequently, an Autoclave Engineers 300 mL stirred autoclave was purchased which would allow us to carry out experiments on relatively small samples of lignins (20-200 g). The autoclave is capable of handling pressures up to 5000 psi at 455°C and has a DC electric stirrer that can be continuously controlled from 0-2500 rpm, thus facilitating examination of the effect of mixing. The system attached to the autoclave shown in Figure 1 is set up so that material may be injected into the reactor after the reactor has been preheated to the desired temperature, resulting in a very rapid heating (400°C can be obtained in under 2 minutes) of the lignin to hydrotreating temperatures. The system has also been designed so that hydrogen flow sweeps volatiles from the autoclave into the collection system. Liquid samples can also be taken from the bottom of the reactor through a dip tube. Volatile products and liquid samples are collected in a pressurized condenser and a second ambient pressure condenser packed with glass wool and maintained at much lower temperatures to knock down any aerosols formed.

This system has all the features we identified from the literature and from our early work as being necessary for hydrotreating to be carried out most effectively. The sample injection system provides rapid heating of the sample; volatile products can be swept from the autoclave and a high rate of mixing can be realized.

Solvent Selection

Lignins are solids and in order for them to be transported through the injection system and for the impeller to impart good mixing to the lignin and catalyst in the autoclave, a solvent or liquid vehicle in which the lignin and catalyst are suspended must be used. Solvent selection must be very carefully made, as an improper choice can greatly distort results obtained. Any solvent or liquid vehicle chosen should be inert to thermal degradation at the temperatures used in hydrotreating. At these temperatures (350°-450°C), it is possible to break some carbon-carbon bonds. Under hydrotreating conditions, it is also possible to cleave most carbon-oxygen bonds and hydrogenate most unsaturated bonds. Because of the

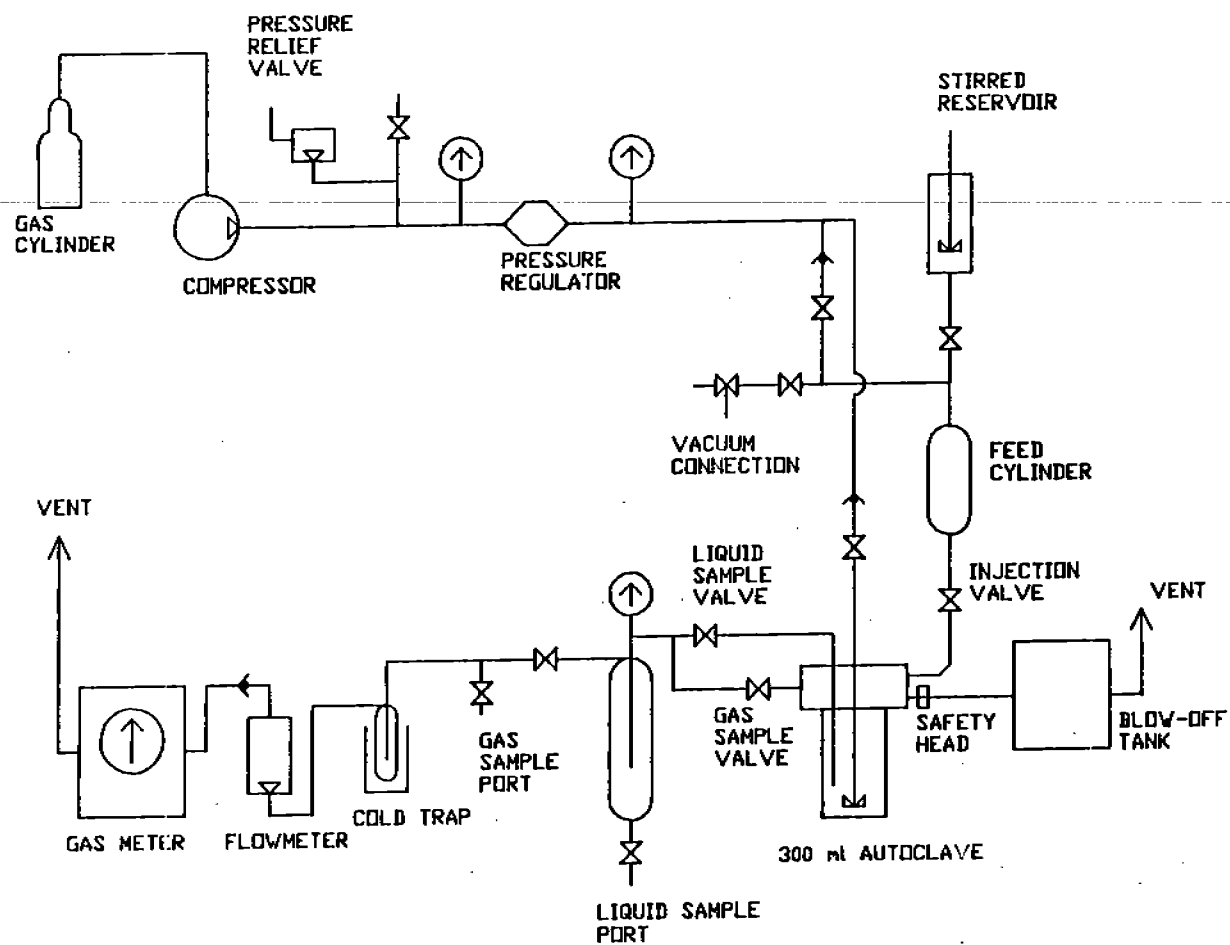


Figure 1. Schematic Layout of the Lignin Hydrotreating System.

stringent conditions of hydrotreating, all common organic solvents in which pretreated lignins are soluble, e.g., methanol, acetone, tetrahydrofuran, etc., cannot be used. Therefore, a liquid vehicle in which the lignins and catalysts can be suspended must be chosen. Another qualification that any vehicle must meet for our hydrotreating experiments is that it should be of lower volatility than the volatile products we intend to sweep from the reactor. The vehicle should remain a liquid in the autoclave to keep the lignin and catalyst suspended.

In the literature on lignin hydrotreating and coal processing, a number of liquid vehicles have been used, most of which appear to have some negative characteristics. 1-Methylnaphthalene is a high boiling liquid that has often been used in coal hydrotreating studies. As reported in our paper at the 1986 Contractors Meeting this liquid vehicle was used in our early studies with the tubing bomb reactor and was found to be unsatisfactory because it was not inert to hydrotreating conditions, only about 75% was recovered. About 5% was demethylated to naphthalene and the remainder was converted to more substituted naphthalenes, e.g., dimethyl naphthalene, because of the ability of the solvent to act as a radical scavenger. In addition, there was always some (10-20%) 1-methylnaphthalene that was swept from the reactor despite its relatively high boiling point (245°C). Tetralin has been used in a number of lignin and model compound hydrotreating studies (eg. Vuori, 1984), but this is a hydrogen donor solvent and also rather volatile. Phenol has also been used as a lignin hydrotreating solvent, but strongly affected the hydrotreating process (Goheen, 1966) and is, again, too volatile. Other pure solvents, e.g., water and hexane, or solvent mixtures, e.g., cresylic acid and paraffin oil, are also unacceptable because of similar reasons.

In the literature, the most effective solvents used were those obtained from lignin. These so-called "pasting oils" were either a recycled portion of the product stream (Gendler, 1983) or a higher boiling fraction from an exhaustively hydrotreated lignin oil (Goheen, 1986). A recycled pasting oil should be considered as partially converted feed, and allowance for this would have to be made in calculating yields. An exhaustively hydrotreated lignin oil might be recoverable or may be converted into volatile products, depending on the severity of the hydrotreating conditions used. In either case, the possibility that the nature of the liquid vehicle is changing as it is reused or as it is recycled from previous experiments must be considered. Another difficulty in using these lignin-derived oils is how to obtain the initial sample of them. Considering the possibilities for solvent or liquid vehicle for lignins, the pasting oils seem to be the only viable option.

As it seems likely that the lignin must be suspended in a liquid vehicle, it was necessary to design the injection system so that it could handle suspensions. Consequently, the valves, fittings, and tubing of the injection system are of 3/8 in. size as far as possible and a mechanical stirrer is fitted to the reservoir. The injection system must also be operated quickly to prevent settling out and plugging once the material is removed from the reservoir and before it is injected.

Testing the Autoclave System

After setting up the system, it was necessary to test our ability to inject a lignin slurry into a preheated autoclave. This had to be accomplished with good mass balance so that the amount injected was accounted for by the amount of liquid, gaseous, and solid (char) products collected.

As catalyst selection is still ongoing, it was decided to test out the system using a hydrogenolysis reaction recently published by Meier et al. (1986). Their process involves the treatment of lignin or wood suspended in water with a palladium (10%) on carbon catalyst and hydrogen at temperatures around 375°C, the critical temperature for water. Meier and co-workers carried out experiments in small tubing bomb reactors that were loaded under ambient conditions and then rapidly heated in a heating block. Our intention was to preheat the reactor empty except for hydrogen at a relatively low pressure and then inject a suspension of lignin and catalyst in water into the reactor with hydrogen at much higher pressure. Because of the relatively high volatility of water, we would not be able to sweep products from the autoclave, but after a set period of hydrotreating, the product would be removed from the autoclave via the dip tube and thus test our ability to quantify the amounts of liquid, solid, and gaseous products formed.

The major product (-60% yield) obtained by Meier et al. (1986) from his experiments with lignin was a brown viscous oil that was soluble in dichloromethane and found to be substantially phenolic. We therefore had an additional interest in trying to repeat this work, as it seemed possible that this might be a method by which we could prepare initial samples of a lignin-derived oil to be used as a pasting oil.

The major difficulty in running these experiments would be that the temperature (375°C) employed is above the critical temperature for water, thus generating a pressure of 3200 psi. With the hydrogen gas that is present, pressures in excess of 4000 psi could be expected. A test of our system under these conditions would ensure that the system could easily handle the 1000 psi or less pressures to be used for lignin hydrotreating.

A dozen hydrogenolysis experiments have now been carried out using lignins from organosolv cooks in addition to several blank runs, made to check the accuracy of our mass balances.

EXPERIMENTAL

Reactor Operation and Isolation of Products

Hydrogenolysis experiments have been carried out on two lignins obtained from aspen wood by aqueous methanol (70:30 methanol:water, 4:1 liquor:wood) organosolv pulping (165°C for 2.5 hrs) using either sulfuric acid (0.05 M, lignin A) or phosphoric acid (0.05 M, lignin B) as pulping catalysts. The details of their preparation are described by Chum et al. (this proceedings). The feed for each experiment constituted lignin (20 g) and the catalyst (2 g, 10% palladium on activated carbon from Aldrich Chemical Co.) suspended in nanopure water (200 mL).

Autoclave Setup. The autoclave was set up and run in a walk-in hood. Before running any experiment, the autoclave system was carefully checked for leaks first by pressurizing with nitrogen and then with hydrogen. Before running experiments with lignin, injections of only water into the autoclave were carried out to check the system for operation at the high pressures generated by water near its critical temperature. It was also determined that the autoclave should be preheated to 440°C to get a temperature of about 375°C after injection.

Autoclave Operation. With the autoclave stirrer set at 1500 rpm the reactor was preheated containing hydrogen at a relatively low pressure (730 psi). The feed mixture was placed in the reservoir where a mechanical stirrer maintained the suspension before being drawn into the previously evacuated feed cylinder. The feed cylinder was then quickly pressurized with 2200 psi of hydrogen which forced the suspension into the autoclave on opening the injection valve. The water was rapidly heated so the injection valve had to be quickly closed to prevent backflow as the steam pressure exceeded the injection pressure. Within two minutes, the temperature stabilized at about 375°C (autoclave pressure was about 4000 psi) and this was maintained for the run time of the experiment. Termination of the experiments occurred when the letdown valve was opened and the aqueous product was withdrawn from the autoclave via the dip tube into the pressurized condenser. Cooling rapidly reduced the system pressure to about 700 psi in one minute. Letdown did not occur from the pressurized condenser until cooling had further reduced the system pressure to about 150 psi. A gas sample (75 mL) was taken and the component gases analyzed quantitatively by gas chromatography. Very little material was collected in the cold trap, and the dry-test meter measured the volume of gas let-down.

Product Workup. The amount of uninjected lignin and catalyst was determined by washing out the stirred reservoir, feed cylinder, and lines to the autoclave. The washings were filtered and the amount of uninjected material was determined after drying. An aqueous emulsion, obtained from the high-pressure condenser, was extracted with ethyl acetate (3 x 150 mL). After extraction the aqueous solution was evaporated to dryness to give the aqueous soluble product. The letdown lines and condenser were then washed out with ethyl acetate, followed by washing with acetone. After the autoclave had cooled to room temperature, it was also washed first with ethyl acetate and then acetone. The washings were first filtered and then evaporated to dryness. The ethyl acetate soluble materials were kept separate from the small amount only soluble in acetone. The ethyl acetate soluble material was a thick, brown oil, while the acetone soluble material was solid. A certain amount of black insoluble material was recovered which after subtraction of the amount of catalyst injected, was designated as the char formed from the reaction. The mass of carbon-containing gas formed was calculated from the measured volume of gas produced and the composition (mole %) of the gas sample analyzed. From these analyses, a mass balance was determined from the amounts of products against the mass of lignin injected. The only products which eluded analysis were any water that might be produced or low-boiling organics, such as methanol.

Product Analyses

Gas Analysis. The gas samples were subjected to a refinery gas analysis on a Carle Analytical Gas Chromatograph 111H using a multicolumn multivalve automated analysis as described in application note No. 156-A of the Carle Series-S (Cat. No. 0156 AGC). This method is capable of determining up to 21 different hydrocarbons and inerts from a single injection. Hydrogen, carbon monoxide, carbon dioxide, methane, ethane, propane, propene, and butane were commonly observed gaseous products.

Volatiles Analysis. The ethyl acetate extracts of the aqueous emulsions collected in the pressurized condenser were analyzed for volatile components using capillary gas chromatography/mass spectrometry on a Hewlett-Packard HP5890/5970 GC/MSD system. The column used was an HP Ultra 1 25 m capillary (0.2 mm ID) column which is coated with a crosslinked methyl silicone gum (0.33 μm thickness, 100% dimethyl polysiloxane). Components are separated using a temperature program from 50 $^{\circ}$ to 300 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$ after holding for 3 minutes at the initial temperature. The injection port was maintained at 250 $^{\circ}\text{C}$ and the transfer line at 280 $^{\circ}\text{C}$. The volatiles found were all phenolic in nature and included phenol, catechol, guaiacol (2-methoxy phenol), syringol (2,6-dimethoxy phenol) and a number of alkyl substituted guaiacols and syringols. The major product was syringol in all but the 45-minute experiments when catechol was the largest component. These products were identified by comparison of their mass spectra with those resident in the library of the system and by comparison with authentic samples.

Gel Permeation Chromatography. The extract and washings were analyzed for their apparent molecular weight distributions using gel permeation chromatography. This was carried out with a Hewlett-Packard HP 1090 liquid chromatograph containing an ultraviolet diode-array detector. A PL Gel GPC column (300 x 7.5 mm) containing 5 μm particles of polystyrene-divinyl benzene copolymer beads with mean pore diameters of 50 \AA was used. Spectroscopic grade tetrahydrofuran was used as eluant at a flow rate of 1 mL/min. Injections (5 μl) were made with an automatic sampler and the column compartment was maintained at 28 $^{\circ}\text{C}$. Elution time was calibrated using polystyrenes and IGEPAL standards of known molecular weight. The details of the technique are described by Johnson and Chum (1987).

RESULTS AND DISCUSSION

Initially, it was decided to test our ability to obtain good mass balances of material injected into the autoclave and then withdrawn into the collection system. The first test was undertaken with the autoclave at room temperature. An aqueous suspension of lignin A in the usual proportions was injected into the autoclave, stirred for 20 minutes, and then withdrawn into the condenser. After going through the usual workup procedure of washings and extraction, 15.9 g of the 16.6 g of injected lignin was recovered, giving a mass balance of 96%. To test our ability to recover material injected into the autoclave heated to hydrotreating temperatures, an aqueous emulsion of 1-methylnaphthalene was chosen because of its relative stability to thermal decomposition at these temperatures. As 1-methylnaphthalene is a liquid immiscible in water, it also allowed us to test our recovery

procedure with a material similar in state to the products we expected from lignin. Workup of the experiment recovered 13.1 g of the 13.3 g of 1-methylnaphthalene injected, a mass balance of 98%. Because of the very good mass balances obtained from these runs, it was felt that good mass balances could be achieved with the lignin hydrogenolysis experiments.

A further blank experiment was run before proceeding to work with lignins, in which only the catalyst and water were subjected to hydrogenolysis. This was performed to determine if any products might be formed from the carbon support of the catalyst. After hydrogenolysis at about 375°C for 20 minutes, nearly all (96%) the catalyst injected into the autoclave was recovered as insoluble material. No ethyl acetate or acetone soluble material was produced. The remainder of the catalyst (4%) was found in a small amount of carbon-containing gases (carbon dioxide, methane, ethane, and propane) that were produced.

Hydrogenolysis experiments with lignins were carried out for 5, 20, and 45 minutes. The majority of the product (50-75 wt % of the lignin injected) in each experiment was found in the ethyl acetate soluble materials of which most was obtained from the washings of the system. This was because the lignin-derived oils did not remain emulsified in the water but would separate out and stick to the walls of the tubing and condenser. The carbon-containing gases were the next largest product fraction occurring in 10-18 wt % of the lignin injected. These gases consisted of carbon monoxide and carbon dioxide in addition to methane, ethane, propane, and propene. These alkanes and alkene can be explained by cleavage from the lignins of methyl groups from the methoxy substituents and of the alkyl side chain that may be up to propyl in size. There were, however, small amounts of butanes and butenes also produced and even occasional traces of pentane. These larger hydrocarbons probably originate from the extractives that are removed with the lignin by the organosolv process. The insoluble material (char) was also produced in significant yields accounting for 3-23 wt % of the lignin injected. The yields of acetone solubles (1-4 wt %) and aqueous solubles (0.2-1.3 wt %) were small in all experiments. Mass balances were better than 84% for all experiments.

Using lignin A, a definite trend was observed in the product yields as a function of run time. As can be seen from Figure 2, the yield of ethyl acetate solubles declined with increasing run time, while carbon-containing gases increased. The yield of insolubles varied between 4 and 13 wt % of the lignin injected but without following any clear trend. Very similar yields and trends were found in two experiments using lignin B run for 5 and 20 minutes. Mass balances also appear to decrease with run time; however, no reason for this has yet been found. It is possible that the products not quantified, water and low-boiling volatiles, could be increasing, but this would be difficult to prove. Reproducibility of results obtained at the same run times appears to be very good. Another experiment using lignin A run for 20 minutes but without any catalyst present clearly showed the beneficial action of the catalyst. The yield of ethyl acetate soluble materials was reduced to 49%, while the yield of insolubles increased to 23% of the lignin injected. The carbon-containing gases (11%), acetone (2%), and aqueous solubles (0.4%) were produced in amounts similar to other experiments. The total mass balance was 85%.

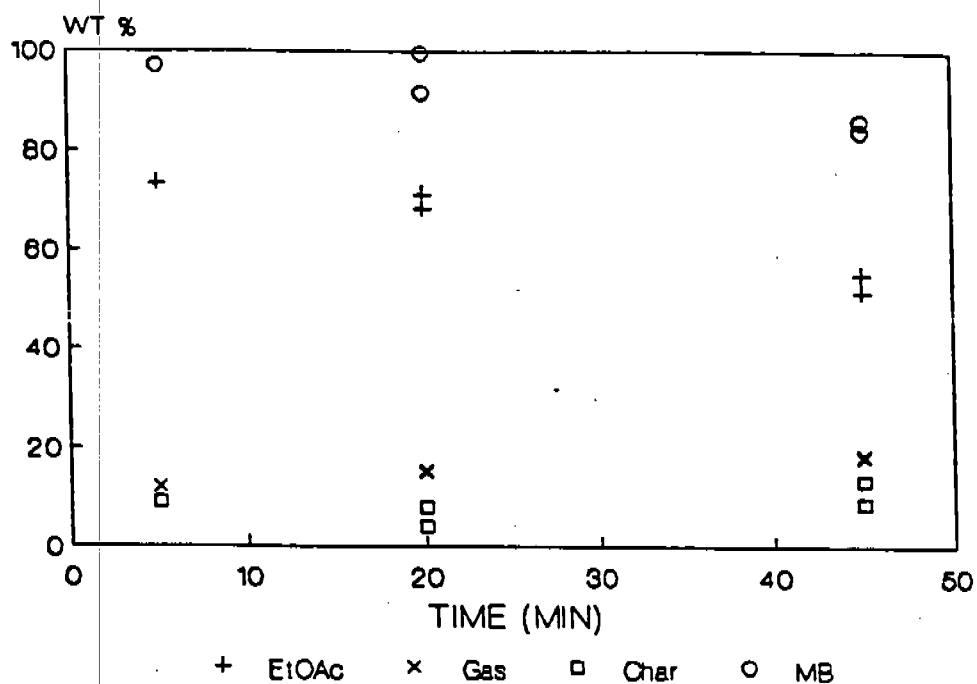


Figure 2. Yields of Ethyl Acetate Solubles (EtOAc), Gases and Insolubles (Char), and Mass Balances (MB) from Hydrogenolyses of Lignin A at Different Run Times.

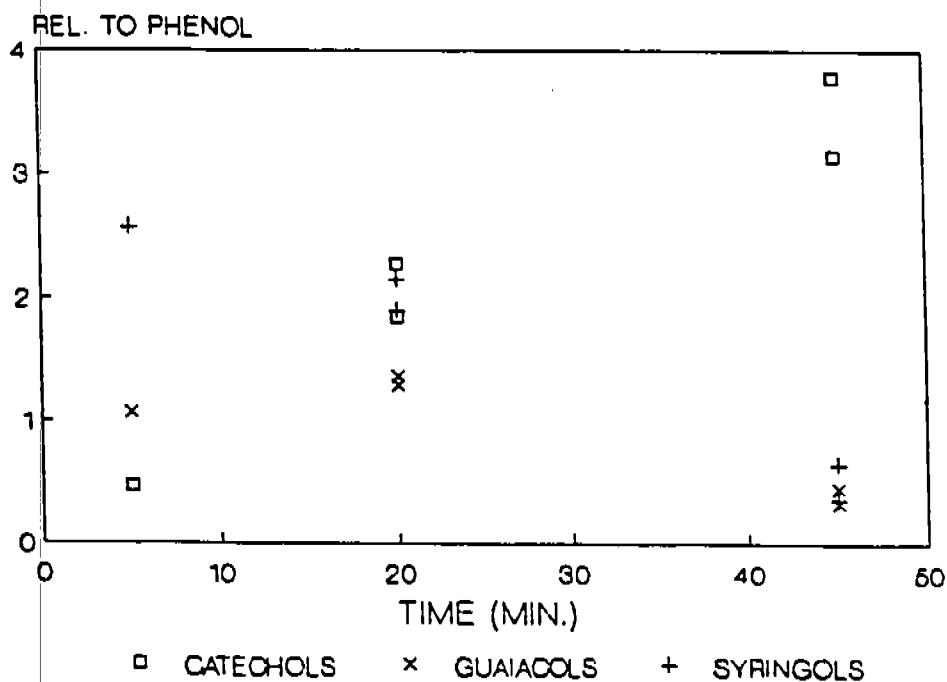


Figure 3. Yields of Combined Catechols, Guaiacols and Syringols, Relative to Phenol, from Hydrogenolyses of Lignin A at Different Run Times.

Volatiles Analysis

Using the GC/MSD, the volatile materials present in the ethyl acetate extracts of the emulsions from the condenser were analyzed. In addition to phenol, three groups of phenolic compounds were identified as being present. There were three catechols identified: catechol (1,2-dihydroxybenzene), methyl catechol, and 6-methoxy catechol; four guaiacols including guaiacol (2-methoxy phenol), 4-methyl, 4-ethyl, and 4-propyl guaiacol; and four syringols including syringol (2,6-dimethoxy phenol), 4-methyl, 4-ethyl, and 4-propyl syringol. Four components remain unidentified with m/e of 154, 182(two), and 212. Meier et al. (1986) found similar phenolics in their hydrogenolyses observing, as expected, only the guaiacols from spruce (a softwood) lignin but phenols, guaiacols, and syringols from bagasse (a grass) lignin. Meier et al. did not, however, report the formation of catechols. The absolute amounts of each phenolic and their total composition in each extract varied widely (15-28 wt % of the extracts) from run to run with poor reproducibility within repeated experiments. However, the ratio of each component to the amount of phenol produced did show a distinct trend with run time and reproduced well in repeated experiments. From Figure 3, it can be clearly seen that relative to phenol, the combined yields of syringols decreased with increasing run time, while the combined yields of catechols increased. The combined yields of guaiacols relative to phenol appear to go through a maximum and then decrease with run time. These results obtained from hydrogenolyses of lignin A were repeated in the two experiments using lignin B, except that the relative amount of syringols produced appears higher. The fact that Meier et al. did not observe any catechols may then be explained because our hydrogenolyses lasted at least 5 minutes (on much larger samples) at 375°C, while theirs were terminated when their reactor reached 375°C, although their lignins were exposed to high temperatures during 15 minutes of heatup. The guaiacols and syringols are formed by depolymerization of the lignin to its alkyl phenol repeating unit. For the lignins used, the repeating units have between one and two methoxys per aromatic and the side chain substitution should be one to three carbons in length. The major product in the 5 and 20 minute experiments was syringol, indicating that some cleavage of the alkyl side chain has taken place. The increase in guaiacols formed at 20 minutes indicates a step-wise degradation of syringols to guaiacols by demethoxylation. In addition, guaiacols should also be produced by direct degradation of lignin. The catechols were formed by demethylation which increased as the run time increased. In making these inferences it must be remembered that the volatiles only represent 2.4 to 5.7% of the lignin injected into the autoclave.

GPC Analyses

The gel permeation chromatographic analyses are used to reveal the molecular weight distributions of the various fractions obtained from each experiment. In all cases, the products obtained are reduced in apparent molecular weight compared to the starting lignins. Lignin A was lower in apparent molecular weight (weight average molecular weight M_w = 940) than lignin B (M_w = 1700). The ethyl acetate soluble fractions obtained after hydrogenolysis of these lignins have apparent molecular weights of about 500. From the GPC of the individual fractions from each experiment, no

clear trends can be seen of the effect of run time on depolymerization; however, it is clear that the ethyl acetate extract is generally lower in apparent molecular weight than the washes, with the reactor washes normally having the highest molecular weights. The acetone washes also contain higher apparent molecular weight materials than the ethyl acetate washes.

Summary

Hydrogenolyses have been run in the autoclave system, and the equipment has performed well under conditions of much higher pressure than envisioned for the lignin hydrotreating experiments. The injection system worked well in handling the aqueous lignin suspension, and good mass balances were obtained from a number of blank runs and from the lignin hydrogenolysis experiments, especially those of short run time. The hydrogenolysis process proved capable of producing a lignin-derived oil in good yield (~70%) that may be suitable for use as an initial lignin pasting oil in future lignin hydrotreating experiments. The lignin-derived oil is phenolic in nature (conductimetric titration of one sample found 6 wt % of phenolic hydroxy groups, increased from the 4.9 wt % of the starting lignin), and the apparent molecular weights of these oils are greatly decreased from those of the starting lignins.

FURTHER WORK

The work planned for the immediate future is to carry out experiments in which volatiles are swept from the autoclave, under hydrotreating conditions, into the collection system. A wood pyrolysis oil obtained from the SERI fast pyrolysis reactor, will be used as feed with the palladium on carbon catalyst used previously. This will allow us to test our ability to hydrotreat a complex feed with the rapid removal of volatile products which should contain substantial amounts of phenols. As before, our ability to carry out these experiments with good mass balance of products against material injected into the autoclave will be very important. The advantage of using this pyrolysis oil is because it is a liquid, no pasting oil will be necessary.

In the near future, it is important that sufficient pasting oil be generated so that operation of the autoclave system with lignin suspended in a pasting oil can be tested. The initial sample of pasting oil may be generated by hydrogenolysis of lignin or possibly from the products of hydrotreating the pyrolysis oils.

The catalysts currently being developed as another part of this task all require a sulfidization pretreatment, preferably in situ. In the near future, it will be necessary to develop and test out a procedure for this pretreatment that can be carried out in the autoclave system. A suitable catalyst for lignin hydrotreating should be selected during 1988. It is, therefore, expected that lignin hydrotreating experiments will be carried out in the autoclave system before too long. In addition, in collaboration with N. Hinman (Biotechnology Research Branch) a preliminary economic evaluation of lignins to methyl aryl ethers will be carried out.

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